Novella, D., Dolejš, D., Myhill, R., Pamato, M. G., Manthilake, G., & Frost, D. J. (2017). Melting phase relations in the systems Mg2SiO4-H2O and MgSiO3-H2O and the formation of hydrous melts in the upper mantle. *Geochimica et Cosmochimica Acta*, *204*, 68-82. https://doi.org/10.1016/j.gca.2016.12.042

# Melting phase relations in the systems $Mg_2SiO_4$-$H_2O$ and $MgSiO_3$-$H_2O$ and the formation of hydrous melts in the upper mantle

Davide Novella [a,b,c*], David Dolejš [d,e], Robert Myhill [a,f], Martha G. Pamato [a,g], Geeth Manthilake [a,b] and Daniel J. Frost [b]

[a] Bayerisches Geoinstitut, Universität Bayreuth, Universitätsstrasse 30, D-95447 Bayreuth, Germany

[b] Laboratoire Magmas et Volcans, Université Blaise Pascal, 5 Rue Kessler, 63038 Clermont-Ferrand, France

[c] Lawrence Livermore National Laboratory, Livermore, California 94550, USA

[d] Institute of Petrology and Structural Geology, Charles University, Albertov 6, CZ-12843 Praha 2, Czech Republic

[e] Present address: Institute of Earth and Environmental Sciences Albert-Ludwigs-University of Freiburg, Albertstrasse 23b, D-79104, Freiburg, Germany

[f] Present address: School of Earth Sciences, University of Bristol, Queens Road, BS8 1RJ, Bristol, UK

[g] Present address: Department of Earth Sciences, University College London, Gower Street, WC1E 6BT, London, UK

[*] Corresponding author. E-mail: dn345@cam.ac.uk; Tel: +44 1223 768327

Present address: Department of Earth Sciences, University of Cambridge, Downing Street, CB2 3EQ, Cambridge, UK

**Abstract**

High-pressure and high-temperature melting experiments were conducted in the systems $Mg_2SiO_4$-$H_2O$ and $MgSiO_3$-$H_2O$ at 6 and 13 GPa and between 1150 to 1900 °C in order to investigate the effect of $H_2O$ on melting relations of forsterite and enstatite. The liquidus curves in both binary systems were constrained and the experimental results were interpreted using a thermodynamic model based on the homogeneous melt speciation equilibrium, $H_2O + O^{2-} = 2\ OH^-$, where water in the melt is present as both molecular $H_2O$ and $OH^-$ groups bonded to silicate polyhedra. The liquidus depression as a function of melt $H_2O$ concentration is predicted using a cryoscopic equation with the experimental data being reproduced by adjusting the water speciation equilibrium constant. Application of this model reveals that in hydrous $MgSiO_3$ melts at 6 and 13 GPa and in hydrous $Mg_2SiO_4$ melts at 6 GPa, water mainly dissociates into $OH^-$ groups in the melt structure. A temperature dependent equilibrium constant is necessary to reproduce the data, however, implying that molecular $H_2O$ becomes more important in the melt with decreasing temperature. The data for hydrous forsterite melting at 13 GPa are inconclusive due to uncertainties in the anhydrous melting temperature at these conditions. When applied to results on natural peridotite melt systems at similar conditions, the same model infers the presence mainly of molecular $H_2O$, implying a significant difference in physiochemical behavior between simple and complex hydrous melt systems. As pressures increase along a typical adiabat towards the base of the upper mantle, both simple and complex melting results imply that a hydrous melt fraction would decrease, given a fixed mantle $H_2O$ content. Consequently, the effect of pressure

on the depression of melting due to $H_2O$ could not cause an increase in the proportion, and hence seismic visibility, of melts towards the base of the upper mantle.

**Keywords:** olivine, enstatite, phase equilibria, hydrous melting, cryoscopic equation, water speciation.

## 1. Introduction

The effect of $H_2O$ on the formation of silicate melts underlies a number of igneous processes taking place within the Earth's mantle. $H_2O$ has an important influence on the generation of magmas at subduction zones being both a metasomatic agent of the arc magma source region and responsible for the high degrees of melting that produce these magmas (e.g. Tatsumi et al., 1986). The lithospheric mantle shows abundant evidence for metasomatism by $H_2O$-bearing melts (e.g. Menzies and Hawkesworth, 1987; Erlank et al. 1987) and several exotic magma types such as kimberlites and lamproites are likely formed, at least in part, as a result of $H_2O$ lowering the mantle solidus (e.g. Kushiro et al., 1968; Kawamoto and Holloway, 1997; Sokol et al., 2013). $H_2O$ induced melting of the deep mantle has also been proposed to explain a number of geophysical observations such as the Earth's seismic low velocity zone (Lambert and Wyllie, 1970; Mierdel et al., 2007) and possible low velocity layers present on top of the transition zone (Tauzin et al., 2010) and immediately below it (Schmandt et al., 2014). Recently, it was proposed that $H_2O$-induced melts would tend to migrate in the lower mantle, and transfer $H_2O$ from ultramafic to mafic lithologies, as a result of the difference in $H_2O$ storage capacities of these rock types (Pamato et al., 2015).

In order to understand the production of hydrous melts in the Earth's mantle it is important to constrain how $H_2O$ affects the melting behaviour of mantle materials. In this regard, a number of studies have been performed to quantify the effects of $H_2O$ on lowering melting temperatures and increasing melt yields in natural mantle rock systems (Mysen and Boettcher, 1975; Hirose and Kawamoto, 1995; Gaetani and Grove, 1998; Balta et al., 2011; Tenner et al., 2012b; Novella et al., 2014). Determining the effect of $H_2O$ on melting in natural chemical systems is challenging, however, due to the large number of chemical components that are potentially influenced by $H_2O$. These determinations are further complicated by a number of other instrumental factors, such as control of oxygen fugacity, attainment of equilibrium, $H_2O$ and FeO loss from experimental capsules and the difficulty in determining the $H_2O$ contents of melts (Brooker et al., 1998; Liu et al., 2006; Tenner et al., 2012b; Novella and Frost, 2014).

It has long been appreciated that the effects of $H_2O$ on silicate melts can be more easily quantified by examining melting behavior in simple systems (Kushiro et al, 1968; Kushiro and Yoder, 1969; Kushiro, 1972; Hodges, 1973, 1974). From results of experiments in simple systems such as $Mg_2SiO_4$-$SiO_2$-$H_2O$, Kushiro (1972) proposed, for example, that hydrous mantle partial melts would be more $SiO_2$-rich compared to dry melts. Studies in simple systems can also be used to quantify the effect of $H_2O$ on mineral melting at high pressures and experiments have been performed up to conditions equivalent to those in the mantle transition zone (Kushiro and Yoder, 1969; Luth, 1993; Inoue, 1994). While relatively detailed melting phase relations on hydrous forsterite

92 (Kushiro and Yoder, 1969; Hodges 1973) and enstatite (Kushiro and Yoder, 1969;
93 Kushiro et al., 1968) exist up to 3 GPa, phase relations at higher pressures are more
94 sparse and show less mutual agreement. Luth (1993) and Inoue (1994) investigated the
95 melting behavior of forsterite with 17-20 wt% $H_2O$ up to pressures of 12 and 15.5 GPa,
96 respectively, although the two studies are in poor agreement. In addition, Inoue (1994)
97 also studied the phase relations of hydrous enstatite and an intermediate Mg/Si ratio
98 composition to similar pressures. However, in this previous study more emphasis was
99 placed on determining the conditions of the hydrous solidus rather than quantifying the
100 effect of melt $H_2O$ content on the melting temperature.
101
102 Recently, several studies on natural multicomponent systems have proposed generalized
103 models for the effects of $H_2O$ on peridotite melting temperatures (Medard and Grove,
104 2008; Tenner et al., 2012a). While such models are quite successful in reproducing the
105 experimental observations, they make assumptions concerning both the thermodynamic
106 data and the mechanism by which $H_2O$ dissolves in melts that can be more easily tested
107 using results on simplified systems. In simplified systems additional constraints are also
108 provided by calorimetric measurements such as those performed to determine the entropy
109 of melting (Bottinga, 1985; Navrotsky et al., 1989; Richet et al., 1993; Tangeman et al.,
110 2001). One advantage of examining experiments in simple systems is that treatment with
111 relatively simple thermodynamic models should provide a firmer basis for understanding
112 hydrous melting on a physicochemical level (Burnham, 1975; Silver and Stolper, 1985)
113 and can be used to examine how the effect of $H_2O$ on melting may be further modified by
114 pressure.

The goal of this study is to determine the melting phase relations in the systems $Mg_2SiO_4$-$H_2O$ and $MgSiO_3$-$H_2O$ at upper mantle conditions. In particular, we investigate the $H_2O$ contents of melts in equilibrium with forsterite and/or enstatite as a function of temperature at high pressure by bracketing the location of the hydrous liquidus curves. The experimental data are analysed using thermodynamic models to provide insight into the $H_2O$ dissolution mechanism and its effects at high pressures. Results are presented for both systems at 6 and 13 GPa corresponding to ~180 and ~390 km depth in the mantle, and temperatures ranging between 1150 to 1900 °C.

## 2. Experimental and analytical details

Two sets of compositions were prepared for experiments in the systems $Mg_2SiO_4$-$H_2O$ and $MgSiO_3$-$H_2O$. In the system $Mg_2SiO_4$-$H_2O$, starting compositions were mixed from two end-member compositions: $Mg_2SiO_4$ (forsterite) synthesized from high purity oxides, MgO and $SiO_2$, and a 2:1 molar mixture of $Mg(OH)_2$ (brucite) and $SiO_2$. The pure forsterite was synthesized by firing the oxides at 1500 °C for 2 hours and then grinding the sintered mix for 1 hour under ethanol. This firing and grinding process was repeated 4 times. The 2:1 brucite-silica mixture corresponds to a composition of $Mg_2SiO_4$ with 20.4 wt% $H_2O$ in the bulk. In order to prepare this end member, brucite and $SiO_2$ were dried overnight at 120 °C and 1000 °C, respectively. The calculated amount of each component was then weighed, ground for 1 hour under ethanol and dried under an infrared lamp. By varying the mass proportions of the end member compositions a range of mixtures were prepared with variable $H_2O$ content but with a constant stoichiometry of Mg/Si= 2 (Table

1). All mixtures with water contents less than 20.4 wt% were prepared by grinding the weighed proportions of dry forsterite and forsterite with 20.4 wt% bulk $H_2O$ for 30 minutes under ethanol, and then drying. Before each mixture was prepared the forsterite end-member was dried at 1000 °C for one hour and the water-bearing forsterite end-member was dried overnight at 120 °C. This approach was also followed for the preparation of starting mixtures in the system $MgSiO_3$-$H_2O$. In this case, an end-member 1:1 molar mixture of brucite and $SiO_2$, corresponding to a composition of $MgSiO_3$ with 15.2 wt% bulk $H_2O$, was initially prepared (Table 1). The dry end-member $MgSiO_3$ was prepared from high purity oxides MgO and $SiO_2$ and the dry and hydrous end-members were mixed in different mass proportions to obtain the compositions given in Table 1. Once prepared, all final mixtures were stored in a furnace at 120 °C to limit the adsorption of water.

Platinum or platinum/rhodium multi-chamber capsules were fabricated from 2 mm diameter Pt or Pt/Rh ($Pt_{90}Rh_{10}$) rods cut into 1 mm long sections. The resulting discs were spark eroded on one surface, obtaining rows of 4 to 6 chambers per disc with the chambers being 0.25 mm in diameter and approximately 0.66 mm deep. Each chamber was loaded with a different starting powder such that $H_2O$ contents increased across the row of chambers. Sample powders were packed into each chamber using a tungsten-rhenium needle. When packed sufficiently the chambers remained full even when air was blown over the surface. Blowing air removed extraneous sample powders from chambers that had not yet been loaded. The Pt capsules were closed by placing a second Pt disc 0.25 mm thick on top of the chambers, which was held closed under pressure. When Pt/Rh capsules were employed the open extremities of the chambers were closed by placing on top 6 foils of Pt/Rh with total thickness of ~0.25 mm.

High pressure and high temperature experiments were carried out using a multianvil apparatus installed at the Bayerisches Geoinstitut (BGI). The experiments were performed in an 18/11 assembly, with an 18 mm edge length $Cr_2O_3$-doped MgO octahedral pressure medium and 11 mm WC-anvil corner truncations. Experiments at 6 GPa were performed using a 500 tonne Walker-type multi anvil press and a 5000 tonne Kawai-type multianvil press. The experiments at 13 GPa were carried out only with the 5000 tonne multianvil apparatus. The pressure calibration at 6 GPa was performed using the $CaGeO_3$ garnet to perovskite phase transition (Ross et al, 1986) for the 500 tonne multianvil apparatus, while the pressure calibration described by Frost et al. (2004) was

173 employed for the experiments performed with the 5000 tonne press. A stepped graphite
174 heater was used in the experiments at 6 GPa, while for those performed at 13 GPa a
175 stepped $LaCrO_3$ heater was employed. Temperatures during the experiments were
176 monitored using a $W_{97}Re_3$–$W_{75}Re_{25}$ (D type) thermocouple inserted within an alumina
177 sleeve. The thermocouple junction was in contact with the base of the spark eroded
178 capsules, ~0.5 mm from the sample chambers, with an estimated temperature uncertainty
179 of 50 °C (Frost et al., 2004). However, higher uncertainty (100 °C) is considered for
180 experiments where the thermocouple reading failed and temperature was determined
181 based on power-temperature calibrations. A 25 μm thick foil of rhenium was placed on
182 the top of the capsule in order to avoid direct contact between the capsule and the
183 thermocouple junction. The maximum temperature fluctuation during the experiments
184 was ± 5 ºC. The capsule was surrounded by MgO spacers and sleeves. Each experiment
185 was first pressurised over 4 hours then heated in ~15 minutes to target temperature where
186 it remained for up to 30 minutes depending on target temperature. Once completed, the
187 experiment was quenched by turning off the power supply to the graphite/$LaCrO_3$ heater,
188 and decompression was carried out over approximately 15 hours.
189
190 After each experiment, the Pt or Pt/Rh sample disk was recovered, mounted in epoxy and
191 polished in the absence of water. Due to the high porosity of the charges, impregnation
192 with either epoxy resin or superglue was often required in order to avoid loss of material
193 during the polishing. Once the samples were polished, phase identification and chemical
194 analyses were carried out using a JEOL-JXA-8200 electron microprobe (EMPA) at the
195 BGI. Conditions of 15 kV and 15 nA for the accelerating voltage and beam current,

196 respectively, were adopted in all the analyses, using a beam diameter of ~1 μm. Standards
197 for $SiO_2$ and MgO were forsterite and enstatite, respectively, and all the analyses were
198 processed following the ZAF corrections.
199
200 Raman spectroscopy was conducted on some of the experimental charges to confirm the
201 nature of the mineral phases produced. The analyses were performed using a LABRAM
202 Raman spectrometer installed at the BGI and operating with a He-Ne laser with 632 nm
203 red-line wavelength. Analyses were performed with a total of 3 spectrum collections and
204 an accumulation time of 15 seconds each.
205
206 **3. Results**
207 Sections of typical experimental runs are shown in Fig. 1. At both pressures of 6 and 13
208 GPa melts quenched to produce a fine intergrowth of crystals. However, crystals that
209 were solid phases during heating of the experiments were easily distinguished from the
210 quenched crystals based on their euhedral character and grain size. In some experiments
211 quenched areas with different grain sizes and crystallite shapes could be observed that
212 might be interpreted as separate coexisting liquids, or vapour (Fig. 1a). Given that the
213 $H_2O$ contents of the charges are relatively low for fluid-saturated conditions to be
214 encountered (e.g. Mibe et al., 2002), it seems more likely that these differences in texture
215 result from local differences in nucleation and growth during quenching of the
216 experiments. All quench textures are consistent with an origin as $H_2O$-bearing melts
217 rather than aqueous fluids. This distinction is made based on the quench crystal density

compared to previous studies performed at lower temperatures where a sub-solidus aqueous fluid phase was encountered (Mibe et al. 2002).

Sections were ground by hand to over half way through the sample chambers to verify the absence of crystals in experiments interpreted to have encountered superliquidus conditions. Continual checks were made during grinding to examine for crystals that might not otherwise appear in the final section. Some samples were ground more than 80% through to ensure that no crystals were present in the charge. The small size of the sample chambers should ensure that thermal gradients across the samples are minimal. The large relative size of the metal capsule should also help to relax thermal gradients. Based on measurements performed in similar assemblies using two pyroxene thermometry (Brey et al., 1990), the thermal gradients within each chamber are estimated to be <20 °C.

Several experiments were performed at the same conditions but with different heating durations in order to assess $H_2O$ loss from the Pt capsules during the experiments. Two experiments loaded with the same starting mixtures were performed at 6 GPa and 1400 ºC for 5 and 30 minutes, respectively, and in both cases the resulting assemblages in each of the sample chambers were identical. At 13 GPa the same result was obtained in two experiments performed at 1450 ºC. These observations imply that significant loss of $H_2O$ does not occur in experiments with run durations up to 30 minutes at temperatures up to 1450 °C. However, it was observed that in some experiments performed at higher temperatures (>1650 ºC), run durations greater than 30 minutes led to substantial

241 crystallisation, likely due to $H_2O$ loss from the Pt capsule. Therefore, experiments
242 performed above 1650 °C were held at target temperature for 5-20 minutes only.
243
244 **3.1 Experimental results at 6 GPa**
245 Experimental conditions and phase assemblages of the runs performed at 6 GPa for both
246 $Mg_2SiO_4$-$H_2O$ and $MgSiO_3$-$H_2O$ systems are summarized in Table 2. In the forsterite-$H_2O$
247 system, experiments were performed from 1250 to 1650 ºC (Fig. 2). In some runs
248 performed at 1250 ºC crystals of enstatite were also observed, possibly suggesting
249 incongruent melting at these conditions. However, this observation is not in agreement
250 with the experimental results of Inoue (1994), which indicate the transition from
251 congruent to incongruent melting of forsterite in the system $Mg_2SiO_4$-$H_2O$ to occur
252 between 7.7 and 12 GPa. Rather than incongruent melting, the appearance of enstatite is
253 possibly due to slight variations of certain starting mixtures from the Fo-$H_2O$ join, which
254 would be more visible at high degrees of crystallization. Our data suggest that the
255 invariant curve Fo + En = Liquid is passing very close to the fo-$H_2O$ line and possibly
256 crossing it (Fig. 3), explaining the observed phase relations (Table 2). In experiments
257 conducted at temperatures above 1250 ºC, the run products contained either forsterite and
258 melt or melt only, implying congruent melting. The run with the highest $H_2O$ content
259 (20.4 wt%) produced crystals in equilibrium with quenched melt at 1250 ºC, hence it had
260 not yet reached the liquidus temperature (Table 2). However, at temperatures higher than
261 1250 ºC, most experiments had one or more chambers that contained a supraliquidus
262 product that comprised only quenched melt. At 1400 ºC, for example, forsterite crystals
263 coexisting with melt were produced in charges with $H_2O$ contents of 7.9, 9.7, 13.8 wt%,

but the run with 18.3 wt% $H_2O$ contained only hydrous melt (Fig. 1b, Table 2). The proportion of crystals in each of these runs decreases in agreement with the lever rule as the crystal-melt region is crossed as a function of $H_2O$ content in the system. No interpretation of these proportions is made, however, as it may be inaccurate due to the particular sample section obtained during polishing.

In the $MgSiO_3$-$H_2O$ system, experiments were carried out from 1050 ºC to 1650 ºC, with starting mixtures containing up to 15.2 wt% $H_2O$ (Table 2, Fig. 4). All run products contained enstatite and melt or melt only, indicating that melting occurred congruently over the entire temperature range. In one experiment (V704, Table 2) a tiny crystal of forsterite was found as an inclusion in a large enstatite crystal, but this was most likely a consequence of chemical inhomogeneity in the starting mixture. The enstatite liquidus is bracketed at 1650 °C at ~10 wt% $H_2O$ and at 1500 °C at ~15 wt% $H_2O$.

**3.2 Experimental results at 13 GPa**

Experimental conditions and phase assemblages observed at 13 GPa for both systems $Mg_2SiO_4$-$H_2O$ and $MgSiO_3$-$H_2O$ are summarized in Table 3. Experiments were performed between 1300 and 1900 °C. In the $Mg_2SiO_4$-$H_2O$ system, forsterite was found to melt incongruently to an assemblage containing enstatite, forsterite and hydrous melt at temperatures below 1600 °C (Fig. 5). However, the congruent forsterite liquidus could be bracketed at 1700 °C between 13.8 and 20.4 wt% $H_2O$ and at 1900 ºC between 5 and 13.8 wt % $H_2O$ (Table 3). At 1300 °C, for example, the formation of forsterite in equilibrium with melt was observed at the highest bulk water contents (20.4 wt%), while enstatite was

287 also crystallized at lower bulk $H_2O$ contents. This is possibly due to the fact that the
288 univariant Fo + En = Liquid curve has moved closer to the Fo-$H_2O$ join and small
289 variations within the bulk composition causes enstatite to crystallize (Fig. 3). At 1500 °C,
290 the $Mg_2SiO_4$ plus 5 wt% $H_2O$ starting mixture produced forsterite and melt along with
291 minute crystals of MgO (estimated to be <1 vol%). The lower temperature of this
292 experiment compared to others where MgO was not observed implies that the MgO
293 crystals most likely formed due to a slight inhomogeneity in the starting mixture, rather
294 than an incongruent melting reaction. As we do not observe the presence of MgO in any
295 other of the experiments it is likely that the Fo + Per = Liquid univariant curve crosses
296 the Fo-$H_2O$ join at lower $H_2O$ contents than studied (Fig 3), which can be then roughly
297 constrained using the study of Presnall and Walter (1993).
298
299 In the system $MgSiO_3$-$H_2O$, enstatite melted congruently at 1900 ºC and the liquidus
300 curve was bracketed at this temperature between 4.3 and 10 wt% $H_2O$ (Fig. 6). However,
301 in some of the experiments performed between 1300 and 1700 ºC, the formation of small
302 crystals of stishovite occurred along with enstatite and melt, in agreement with
303 observations of Yamada et al. (2004) at 13.5 GPa. The presence of stishovite may be due
304 to the fact that En + St + L univariant curve has moved near to the En-$H_2O$ join, or even
305 crossed it (Fig. 3). This phase, however, was observed only as a minor component, ~2 vol
306 %, and is, therefore, not expected to cause significant departures from the determined
307 phase relations. Additionally, the enstatite liquidus curve was bracketed at 1700 ºC
308 between 6.2 and 11.8 wt% $H_2O$. At 1600 °C, the most $H_2O$-rich charge (15.2 wt% $H_2O$)

produced an assemblage of enstatite plus melt, which constrains the minimum $H_2O$ concentration of the liquidus melt at this temperature.

## 4. Discussion

### 4.1 Model for hydrous melting of $Mg_2SiO_4$ and $MgSiO_3$

A number of studies have examined the melting point depression of silicate minerals as a function of $H_2O$ content in the melt using the cryoscopic equation (e.g. Silver and Stolper 1985; Medard and Grove, 2008; Hirschmann et al., 2009; Myhill et al., 2016). For $Mg_2SiO_4$ at the liquidus, for example,

$$\ln a^{\text{melt}}_{\text{Mg}_2\text{SiO}_4} = \frac{-\Delta_{\text{m}} G^{\text{o}}}{RT} \quad (1)$$

where $\Delta_m G^o$ is the standard state Gibbs free energy of melting of pure forsterite (see Appendix) and $a^{\text{melt}}_{\text{Mg}_2\text{SiO}_4}$ is the activity of the $Mg_2SiO_4$ component in the binary $Mg_2SiO_4$-$H_2O$ melt. At temperatures below the pure forsterite melting point, $\Delta_{\text{m}} G^{\text{o}}$ can be determined by integrating the entropy of melting of pure $Mg_2SiO_4$, $\Delta_m S^o$, between the temperature of interest, $T$, and the anhydrous melting point, $Tm$. Assuming that $\Delta_{\text{m}} S^{\text{o}}$ is constant with temperature, Eq. (1) becomes:

$$\ln a^{\text{melt}}_{\text{Mg}_2\text{SiO}_4} = \frac{\Delta_{\text{m}} S^{\text{o}} (T - T_{\text{m}})}{RT}. \quad (2)$$

330

331 The standard entropies of melting for $Mg_2SiO_4$ and $MgSiO_3$ solid phases have been
332 derived from calorimetric measurements at 1 bar (e.g. Navrotsky et al. 1989; Richet et al.,
333 1993) and expressions for $\Delta_m S^o$ at higher pressures can be determined from data on the
334 anhydrous melting curves combined with equations of state for solid and liquid $Mg_2SiO_4$
335 or $MgSiO_3$ (see Appendix).

336

337 Use of the cryoscopic equation requires a plausible relationship between the activity and
338 concentration of silicate species in the hydrous melt, which will depend on the $H_2O$
339 concentration in the melt and its dissolution mechanism. Empirical molecular mixing of
340 $Mg_2SiO_4$ or $MgSiO_3$ and $H_2O$ does not produce a sufficient depression of the liquidus to
341 explain the experimental data and it has long been recognized that upon dissolution in
342 silicate melts $H_2O$ dissociates into hydroxyl groups bonded to the silicate framework
343 (Burnham 1975, 1979, 1994; Stolper, 1982; Silver and Stolper, 1989; Zotov and Keppler,
344 1998), i.e.

345

346 $$H_2O + O^{2-} = 2\ OH^-. \qquad (3)$$

347

348 Spectroscopic analyses indicate that both molecular $H_2O$ and $OH^-$ groups are present in
349 silicate melts (e.g. Stolper, 1982, Dixon and Stolper, 1995), and their properties are
350 temperature-dependent (Nowak and Behrens, 1995; Zotov and Keppler, 1998). Silver and
351 Stolper (1985) proposed a thermodynamic model to describe the effects of $H_2O$
352 speciation on the activity of silicate melt components. They assumed that all three species

353 ($H_2O$, $O^{2-}$ and $OH^-$) mix ideally following a homogeneous melt equilibrium (Eq. 3). The
354 activity of the silicate component, $a^{melt}_{Mg_2SiO_4}$, is related to the mole fraction of non-
355 protoned oxygen atoms in the melt, $X^{melt}_{O^{2-}}$, through the expression
356
357 $$a^{melt}_{Mg_2SiO_4} = (X^{melt}_{O^{2-}})^r \quad (4)$$
358
359 where *r* is the number of oxygen atoms available for protonation and mixing per formula
360 unit of silicate, with the chosen formula unit being consistent with the value of $\Delta_m S^o$.
361 Setting r=4 for $Mg_2SiO_4$ or 3 for $MgSiO_3$ implies that H can bond to any of the oxygen
362 atoms in the silicate melt structure.
363
364 The extent of $H_2O$ dissociation in the silicate melt (Eq. 3) is described by the equilibrium
365 constant *K*,
366
367 $$K = \frac{\left(X^{melt}_{OH^-}\right)^2}{X^{melt}_{H_2O} X^{melt}_{O^{2-}}} \quad (5)$$
368
369
370 Following mass balance,
371
372 $$X^{melt}_{H_2O^{tot}} = X^{melt}_{H_2O} + 0.5 X^{melt}_{OH^-} \quad (6)$$
373

where $X^{melt}_{H_2O^{tot}}$ is the total mole fraction of $H_2O$ in the silicate-$H_2O$ melt. Solving Eqs. (5) and (6) simultaneously, subject to the closure constraint

$$X^{melt}_{H_2O} + X^{melt}_{OH^-} + X^{melt}_{O^{2-}} = 1 \quad (7)$$

yields mole fractions of all three species in the hydrous melt. Substituting Eq. (5) and (6) into Eq. (7) yields

$$X^{melt}_{H_2O^{tot}} = 1 - X^{melt}_{O^{2-}} + \frac{KX^{melt}_{O^{2-}} - \sqrt{\left(KX^{melt}_{O^{2-}}\right)^2 + 4KX^{melt}_{O^{2-}} - 4K\left(X^{melt}_{O^{2-}}\right)^2}}{4} \quad (8)$$

which is evaluated for the fraction of non-protonated oxygen atoms in the melt. The corresponding activity of the silicate melt component is calculated from Eq. (4) and the liquidus temperature is then defined by Eq. (2). In order to compare the results of the model with experimental data, $X^{melt}_{H_2O^{tot}}$ can be converted to $w^{melt}_{H_2O^{tot}}$, the mass fraction of $H_2O$ dissolved in the melt using,

$$w^{melt}_{H_2O^{tot}} = \frac{X^{melt}_{H_2O^{tot}} M_{H_2O}}{X^{melt}_{H_2O^{tot}} M_{H_2O} + \left(1 - X^{melt}_{H_2O^{tot}}\right)\frac{M_{sil}}{r}} \quad (9)$$

where $M_{H_2O}$ is the molar mass of water (18.015 g/mol) and $M_{sil}$ is the molar mass of the silicate formula unit.

### 4.1.1 Liquidus depression at 6 GPa

Fig. 2 shows the experimental results for the forsterite liquidus as a function of melt $H_2O$ content at 6 GPa compared to liquidus calculations using several limiting cases of the thermodynamic model. The thermodynamic data used to determine the anhydrous melting point of $Mg_2SiO_4$ and $\Delta_m S^o$ at the pressure and temperature of interest are listed in Table A (see Appendix and Supplementary Material).

Three different curves for the $Mg_2SiO_4$ liquidus are shown calculated for different values of the dissociation equilibrium constant, $K$. If all $H_2O$ is completely dissociated to $OH^-$ ($K = \infty$), the experimental data at the lowest temperatures are in poor agreement with the model as the experimental liquidus becomes less depressed at high $H_2O$ contents. On the other hand, if all $H_2O$ is dissolved in the molecular form ($K = 0$), the predicted liquidus curve is not in agreement with experimental data at any $H_2O$ concentration. The change in slope of the experimental liquidus implies that $K$ is not constant over the range of experimental temperatures, but must change from a high or infinite value (>50) above 1400 °C to <10 below 1300 °C, i.e. molecular $H_2O$ becomes more important as the $H_2O$ saturated solidus is approached. Variations in $K$ with temperature can be described using the function,

$$\ln K = \frac{a}{T} + b, \qquad (10)$$

416

417 which mimics the enthalpic and entropic contributions to *K*. The experimental data do not
418 provide sufficient constraints to determine the *a* and *b* coefficients in Eq. (10) uniquely
419 due to their high correlation. Values of $a \sim -7000$ K and $b \sim 5.6$ are in reasonable
420 agreement, however, with the data and their uncertainties. A different set, $a = -8000$ K
421 and $b = 8$, recently proposed for alkaline basalt by Lesne et al. (2011) based on
422 spectroscopic measurements would also just fit the experimental uncertainties, but start to
423 diverge at temperatures below 1300 °C. The experimental data can only be used to imply
424 a qualitative, strong dependence of *K* on temperature. Independent *in-situ* spectroscopic
425 data would be required to provide a more accurate estimate of this dependence.

426

427 Although the model is relatively simple, improvements that would provide a significantly
428 better fit to the experimental data are relatively limited, without making the model
429 completely empirical. For example, a slightly better agreement between the liquidus
430 curve and the experimental data at ~1450 °C can only be achieved by decreasing the
431 standard entropy of forsterite melting at 1 bar, which is already near the lower limit
432 derived from calorimetric studies (see Appendix). Non-ideal mixing can be included in
433 the model, however, a simple symmetric mixing parameter between the $Mg_2SiO_4$ and
434 $H_2O$ components produces no significant improvement of the fit. In addition, such terms
435 have been shown to be unnecessary to describe the effect of $H_2O$ on melting at lower
436 temperatures, where non-ideal effects should be even more important (Silver and Stolper,
437 1985).

438

439 We further compare our experimental results with the model of Tenner et al. (2012a),
440 which is based on the limiting case where all $H_2O$ dissolves as $OH^-$. In Fig. 2, the liquidus
441 is calculated according to this model using the same thermodynamic data as above and
442 assuming $r = 4$ (random protonation of all oxygen atoms), which is analogous to using a
443 single-oxygen formula unit for the silicate end-member (Tenner et al. 2012a; their Eqs. 9
444 and 11). The predicted liquidus is substantially different from that obtained from the
445 Silver and Solper (1985) model with $K = \infty$, although both models should be equivalent
446 in describing the liquidus depression when $H_2O$ dissolves completely as $OH^-$. The
447 difference arises in the conversion relationships for the mass fraction of $H_2O$ by Silver
448 and Stolper (1985) and Tenner et al. (2012a). To bring these two models to numerical
449 consistency, the following relationship would have to be used to calculate the mole
450 fraction of $OH^-$ in the melt from the $H_2O$ mass fraction,
451

452 $$X_{OH^-}^{melt} = 2\frac{w_{H_2O^{tot}}^{melt} \Big/ M_{H_2O}}{w_{H_2O^{tot}}^{melt} \Big/ M_{H_2O} + \left(100 - w_{H_2O^{tot}}^{melt}\right) \Big/ M_{sil}}, \quad (11)$$

453
454 rather than the conversion equation proposed by Tenner et al. (2012a). The model of
455 Tenner et al. (2012a) has been found to quite accurately reproduce the liquidus of
456 experiments performed in natural complex systems when silicates are mixed on a 3-
457 oxygen formula basis. However, the model does not reproduce data on $Mg_2SiO_4$ at 6 GPa,
458 regardless of the silicate molecular unit considered, providing an independent
459 confirmation that $H_2O$ upon dissolution in silicate melt incompletely dissociates to $OH^-$.
460

A further complexity in the model would be to consider the possibility that not all of the oxygen atoms in the melt structure are available for protonation but, for example, $r = 1$ or 2 per 4-oxygen formula unit (silicate polyhedron) due to local avoidance or ordering principles. This consideration raises two issues, however. First, it would imply a maximum limit for $H_2O$ solubility in the melt, which appears to be not the case. Second, if the number of oxygen sites, which are accessible for proton bonding became an adjustable parameter and were allowed to change, for example, with the $H_2O$ concentration, the resulting fit parameters would be highly correlated with $K$. These parameters cannot be meaningfully constrained without an independent estimate of $K$. Therefore, the Silver and Stolper (1985) model with temperature-dependent speciation in the melt supported by current estimates for $\Delta_m S^o$ of forsterite and the pressure-temperature melting curve of anhydrous forsterite appears to provide an adequate and well-constrained approximation of the experimental data.

In Fig. 4 experimental results bracketing the $MgSiO_3$-$H_2O$ liquidus at 6 GPa are compared with the same set of models as described above. The model that considers complete dissociation to $OH^-$ ($K = \infty$) agrees with experimental data at the highest temperatures investigated (above 1600 °C). At lower temperatures, the experimental data again imply a shallower liquidus slope that is not consistent with the complete dissociation of $H_2O$ into $OH^-$. On the other hand, mixing with molecular $H_2O$ only ($K = 0$) results in a liquidus curve far outside of the experimental uncertainties. A model that considers variation of $K$ with temperature (Eq. 10) fulfils the constraints imposed by the experiments, although a large range of parameters in this equation can provide an

adequate fit to the data. The curve in Fig. 4 was calculated with values of $a$ = -6000 K and $b$ = 4.5 with $K$ decreasing from ~7 at 2100 °C to ~2 at 1300 °C. In addition, two models from Tenner et al. (2012a) that assume mixing of silicate molecules with 1- and 3-oxygen formula units, respectively, are shown in Fig. 4. The model of Tenner et al. (2012a) based on 1-oxygen per formula unit predicts values within the experimental uncertainties. However, these authors find the best agreement with melting data using natural peridotite composition when a 3-oxygen silicate molecule is assumed but, as shown in Fig. 4, this is in poor agreement with the data in this simple $MgSiO_3$-$H_2O$ subsystem.

Both enstatite and forsterite melting experiments at 6 GPa can be described by Silver and Stolper (1985) models that assume mixing of H on all silicate oxygen atoms and a temperature-dependent dissociation of $H_2O$, which proceeds towards complete $OH^-$ formation above ~1400 °C. It is interesting to note that the mass fraction (wt %) of $H_2O$ in the liquidus melt at a given temperature is nearly identical at 6 GPa for both $MgSiO_3$ and $Mg_2SiO_4$ over the entire temperature range.

**4.1.2 Liquidus depression at 13 GPa**

In Fig. 5 experiments bracketing the $Mg_2SiO_4$-$H_2O$ liquidus at 13 GPa are shown and compared to the same models as described for the results at 6 GPa. The melting of pure $Mg_2SiO_4$ becomes incongruent above 10 GPa, with $Mg_2SiO_4$ reacting to produce MgO and melt at the solidus (Presnall and Walter, 1993). Upon the addition of $H_2O$ to the system, melting becomes congruent between 1700-1900 °C (Table 3). For the purpose of

507 modelling the forsterite liquidus, thermodynamic data for congruent $Mg_2SiO_4$ melting at
508 lower pressures have been extrapolated using the melt model of de Koker and Stixrude
509 (2009) to 13 GPa. Models using complete dissociation into $OH^-$ by Silver and Stolper
510 (1985) with $K = \infty$ and by Tenner et al. (2012a) do not reproduce the experimental data
511 (Fig. 5). The best agreement with the experimental liquidus is found for the limiting case
512 of no dissociation, that is, mixing of molecular $H_2O$ ($K = 0$ or 0.2). There are, however,
513 larger inherent uncertainties in performing this evaluation at 13 GPa arising from the
514 melting temperature assumed for anhydrous $Mg_2SiO_4$. Although the thermodynamic
515 model of de Koker and Stixrude (2009) used here provides some theoretical justification
516 for the extrapolation, the resulting dramatic change predicted in the $H_2O$ speciation most
517 probably arises from resulting inaccuracies in the temperature of metastable forsterite
518 melting. By assuming an anhydrous melting temperature that is 250 °C higher than
519 predicted by the anhydrous melting model, the temperature-dependent model for $K$
520 calibrated at 6 GPa for $Mg_2SiO_4$ can be equally applied at 13 GPa. We conclude,
521 therefore, that it is more likely that the anhydrous melting temperature is in error, than
522 that there is a dramatic shift in $H_2O$ speciation at high pressure. This highlights the
523 problems of examining melting point depression in incongruent systems, which are likely
524 to be even more complex for natural multicomponent systems such as mantle peridotite
525 melts.
526
527 For $MgSiO_3$, the liquidus depression at 13 GPa is consistent with the Silver and Stolper
528 (1985) model for nearly complete dissociation to $OH^-$ in the melt (Fig. 6). While this is in
529 contrast to $Mg_2SiO_4$ at the same pressure, it is in better agreement with the experimental

results at 6 GPa. Introducing a temperature dependence to $K$ is not justified by the data, within the experimental uncertainties. A molecular $H_2O$ model is far outside of the experimental constraints, however, as is the model of Tenner et al. (2012a).

### 4.2 The effect of pressure on liquidus depression due to $H_2O$ in simple and complex silicate systems

The liquidus depression under hydrous conditions in comparison to the anhydrous melting point is shown for both the $MgSiO_3$-$H_2O$ and $Mg_2SiO_4$-$H_2O$ systems at 6 and 13 GPa in Fig. 7. Experimental data of Kushiro et al. (1968) for $MgSiO_3$-$H_2O$ at 1 GPa and between 1375 and 1525 °C are used in order to provide an additional comparison; a value of $K = 0.5$ in the Silver and Stolper (1985) formulation provides a good fit to these data. For $MgSiO_3$, pressure enhances the influence of $H_2O$ in depressing the melting temperature in line with thermodynamic estimates for the entropy of fusion and the anhydrous melting curve of $MgSiO_3$. The effect of pressure on the water-driven melting point depression of $MgSiO_3$ is best explained by an increase in the dissociation of $H_2O$ with increasing pressure, with essentially no molecular $H_2O$ being involved above 1400 °C, at pressures of 6 GPa and higher.

For the $Mg_2SiO_4$-$H_2O$ binary, however, there is an apparent decrease in the effect of $H_2O$ on liquidus depression between 6 and 13 GPa. As discussed above this is most likely caused by an underestimate in the metastable melting temperature of anhydrous $Mg_2SiO_4$, which melts incongruently above 10 GPa. If the anhydrous melting temperature is assumed to be 250 °C higher at 13 GPa, then the effect on liquidus depression is reversed.

553 This implies that the extrapolated melting curve for $Mg_2SiO_4$ is incorrect. The Silver and
554 Stolper (1985) model with values of $K$ = ~0.2 at 2100 °C and approaching 0 at 1300 °C
555 successfully reproduce experimental data of Hodges (1974) at 3 GPa in the forsterite-$H_2O$
556 system. Data at 3 GPa show lower melting temperature depression in comparison to those
557 at 6 GPa, is in agreement with the pressure trend observed in the enstatite-$H_2O$ system
558 and further suggesting a positive effect of pressure on melting temperature depression.
559
560 In Fig. 7, data for the liquidus depression due to $H_2O$ for melts of natural peridotite
561 composition are shown from Tenner et al. (2012a) at 3.5 GPa and Novella and Frost
562 (2014) at 6 GPa. The depression of melting due to $H_2O$ is much smaller for these
563 complex melts compared to either of the simple systems at the same pressure. This
564 difference is partly due the lower anhydrous liquidus temperatures of the natural
565 multicomponent melts. As indicated by Eq. (2) the magnitude of the liquidus depression
566 should increase with the anhydrous melting temperature, as observed in all experiments.
567 In Fig. 7 these data are fitted using a Silver and Stolper (1985) model with molar mass of
568 37 g/mol per single-oxygen formula unit and a $\Delta_m S^o$ = 0.4 J/(K·g) (Tenner et al., 2012a;
569 Kojitani and Akaogi, 1997). A constant value of $\Delta_m S^o$ in Eq. (2) is assumed at all
570 pressures and temperatures and the anhydrous melting temperatures are taken from
571 Walter (1998). The best correspondence with experiments at 3.5 GPa requires a
572 temperature dependent value of $K$, which starts near unity close to the anhydrous melting
573 temperature but decreases to effectively zero below 1200 °C. Although there is only one
574 data point available at 6 GPa the depression of melting is consistent with a similar model
575 as at 3.5 GPa, with the only difference being the anhydrous melting temperature. The

576 Silver and Stolper (1985) model, therefore, implies a much smaller extent of $H_2O$
577 dissociation into $OH^-$ and a greater proportion of molecular $H_2O$ in multicomponent melts
578 when compared to simple systems. This difference may have several origins, however.
579 First, the value of $\Delta_m S^o$ employed for peridotite melt is poorly constrained as it is derived
580 from calorimetric measurements in the CaO-MgO-$Al_2O_3$-$SiO_2$ system at 1 bar (Kojitani
581 and Akaogi, 1997) and it may not suitably account for the effects of pressure and
582 composition. Second, it is possible that certain components present in the natural
583 peridotite melt compositions, such as $Al_2O_3$, cause a reduction in the effect of $H_2O$ on the
584 configurational entropy of the melt. As a result of such distinct behaviour, the effect of
585 $H_2O$ on melting in such simple systems may be quite far away from that in complex
586 mantle melts.
587
588 Although the justification as to how the melt $OH^-$ mole fraction is calculated is somewhat
589 unclear in the model of Tenner et al. (2012a), particularly in relation to the Silver and
590 Stolper (1985) model, it is interesting to note that it does closely predict the liquidus
591 depression for complex peridotitic melts at both 3.5 and 6 GPa. The model is based on a
592 3-oxygen melt described by Eq. (11) and it predicts curves identical to those shown in
593 Fig. 7 using the Silver and Stolper (1985) model for the natural peridotite data at 3.5 and
594 6 GPa. Although only empirical in its nature, it tends to numerically mimic decreasing
595 protonation of the oxygen sites in the silicate melt structure, and it produces a good fit to
596 the natural multicomponent data with fewer adjustable parameters. As there seems to be
597 no clear justification to the way in which the $OH^-$ mole fraction is derived in the Tenner et
598 al. (2012a) model, the predictive capacity may be a coincidence.

599

600 **4.2.1 Hydrous melts along adiabatic temperature gradient**

601 A number of seismic observations appear to show evidence for low shear wave velocities
602 at the base of the upper mantle above the 410 km discontinuity (e.g. Song et al., 2004;
603 Vinnik et al., 2009; Jasbinken et al., 2010; Tauzin et al., 2010). These observations have
604 been proposed to result from the presence of low degree volatile-bearing melts at these
605 depths (Bercovici and Karato, 2003). Assuming that the upper mantle has a constant $H_2O$
606 content, it might be possible to explain the visibility of $H_2O$ induced melting at the base
607 of the upper mantle if pressure enhances melt productivity at these conditions. One way
608 that this might occur is if less $H_2O$ were required to stabilise melts with increasing
609 pressure.

610

611 In Fig. 7 the speciation model of Silver and Stolper (1985) using a temperature-dependent
612 value of *K* varying between ~1 and 0 at 3.5 and 6 GPa is extrapolated to 13 GPa by
613 assuming an anhydrous melting temperature of 1900 °C at this pressure (Takahashi,
614 1986). The model by Tenner et al. (2012a) would predict an identical liquidus depression.
615 The results of this extrapolation are given in Fig. 8, which shows the $H_2O$ content in
616 $MgSiO_3$, $Mg_2SiO_4$ and peridotite melts determined at upper mantle adiabatic temperatures
617 (potential temperature ~1350 °C).

618

619 With increasing pressure the amount of $H_2O$ required to stabilize $Mg_2SiO_4$ melt along a
620 mantle adiabat increases quite substantially between 6 and 13 GPa. This means that for a
621 system with a fixed $H_2O$ content, the percentage of melt will decrease towards conditions

622 of the base of an upper mantle. This effect would work in conjunction with an increase in
623 the forsterite-melt $H_2O$ partition coefficient with pressure (see Hirschmann et al., 2009;
624 Novella et al., 2014), which would also act to decrease the percentage of melting for a
625 given bulk $H_2O$ concentration. By contrast, the $H_2O$ content of a $MgSiO_3$ melt appears to
626 actually decrease slightly between 6 and 13 GPa, which could in theory lead to an
627 increase in the percentage of melting for a fixed $H_2O$ content. However, the decrease in
628 melt $H_2O$ content is small and this effect would be counteracted by an increase in the
629 enstatite-melt partitioning coefficient with pressure, calculated from the literature (Rauch
630 and Keppler, 2002; Yamada et al., 2004; Withers and Hirschmann, 2007; Withers et al.,
631 2011) and melt $H_2O$ content from this study. Peridotite melts are also predicted to require
632 more $H_2O$ to be stable at higher pressures, although the $H_2O$ concentrations tend to vary
633 very little towards the base of the upper mantle similar in fact to $MgSiO_3$. This analysis
634 indicates that there is no evidence for increasing melt productivity due to $H_2O$ towards
635 the base of the Earth's upper mantle, although it has to be recognised that there is some
636 uncertainty as the results for peridotite are being extrapolated above 6 GPa.
637
638 In order for the proportion of hydrous melting to increase and therefore be seismically
639 more visible towards the base of the upper mantle, the bulk mantle at these conditions
640 would need to be significantly enriched in $H_2O$. Such a localized enrichment in $H_2O$ at
641 this depth would require an effective fractionation process to maintain high $H_2O$
642 concentrations at this depth. Bercovici and Karato (2003) proposed that hydrous melts
643 formed under these conditions may be neutrally buoyant and, therefore, separate from the
644 upwelling mantle and concentrate to form a low-velocity zone. Such a separation will

depend on melt density, which in turn will depend on the melt $H_2O$ concentration. Melt density experiments by Matsukage et al. (2005) favour such a scenario, although their $H_2O$ concentrations (~6 wt%) are approximately 50 % of those estimated in this study for natural peridotitic melts at the bottom of the upper mantle (Fig. 8). Following the density systematics of Jing and Karato (2009), partial melts in equilibrium with peridotite at 13 GPa should be much less dense than the surrounding mantle if the $H_2O$ contents in the melt are close to those predicted here (Fig. 8).

**Acknowledgements**

Hubert Schulze, Raphael Njul, Stephan Übelhack, Heinz Fischer, Detlef Krausse and Sven Linhardt are kindly acknowledged for their technical support. The present study was supported by the Elitenetzwerk Bayern international graduate school "Structure, Reactivity and Properties of Oxide Materials". D.N. further acknowledges funding from the French Government Laboratory of Excellence initiative n°ANR-10-LABX-0006, the Région Auvergne and the European Regional Development Fund. This is Laboratory of Excellence ClerVolc contribution number xx. D.D. would like to acknowledge personal support by the Czech Science Foundation Project Nr. 210/12/0986. We thank associate editor Mike Toplis and Mike Walter and an anonymous reviewer for comments that significantly improved the manuscript.

**Appendix: Thermodynamic relations and parameters**

The Mie-Grüneisen equations of state (EOS) were employed to determine the Gibbs energy of melting ($\Delta_m G^o$) of forsterite and enstatite required for the cryoscopic equation

668 in the $Mg_2SiO_4$-$H_2O$ and $MgSiO_3$-$H_2O$ binaries. Expressions to define the Gibbs energy
669 for $Mg_2SiO_4$ and $MgSiO_3$ were taken from Stixrude and Lithgow-Bertelloni (2011) for
670 solids and from de Koker and Stixrude (2009) for liquids and are based on the
671 fundamental thermodynamic relation between the Helmholtz energy (F) and the Gibbs
672 energy:
673
674 $$G(P, T) = F(V, T) + PV, \quad \text{(A.1)}$$
675
676 where $V$ is the volume, $P$ is the pressure and $T$ is the temperature. The Helmholtz energy
677 at elevated pressure and temperature is obtained by stepwise integration from ambient
678 conditions ($T_0$ = 298.15 K, $P_0$ = 101325 Pa) *via* isothermal compression at reference
679 temperature (c) and isochoric heating (th), which accounts for the effect of thermal
680 vibrations:
681
682 $$F(V, T) = F(P_0, T_0) + \Delta F_c(T_0) + \Delta F_{th}(V). \quad \text{(A.2)}$$
683
684 The contribution to the Helmholtz energy due to isothermal compression ($\Delta F_c$) was
685 calculated from the third-order Birch-Murnaghan EOS (Murnaghan, 1937; Birch, 1947;
686 e.g. Poirier, 2000):
687
688 $$\Delta F_c(T_0) = 9K_0V_0\left(\frac{f^2}{2} + \frac{af^3}{3}\right). \quad \text{(A.3)}$$
689

690 The EOS is based on the finite strain theory, where the finite strain (*f*) and the factor *a* are
691 calculated as follows:
692
693 $$f = \frac{1}{2}\left[\left(\frac{V_0}{V}\right)^{2/3} - 1\right] \quad \text{(A.4)}$$
694
695 and
696
697 $$a = \frac{3}{2}\left(K_0' - 4\right). \quad \text{(A.5)}$$
699
700 In this formulation, $K_0$ and $V_0$ correspond to the bulk modulus and the volume,
701 respectively, at the reference pressure and temperature, and $K'_0$ is the first pressure
702 derivative of the bulk modulus at reference conditions. The volume ($V$) of the phase at the
703 pressure and temperature of interest was found in order to satisfy the following relation:
704
705 $$P = P_c + P_{th}\ , \quad \text{(A.6)}$$
706
707 where
708
709 $$P_c = 3K_0 f(2f+1)^{5/2}(1+fa). \quad \text{(A.7)}$$
710

711 The equations of state for thermal pressure ($P_{th}$) and calculation of the relevant
712 thermodynamic properties differ for liquid and solid phases. For the liquid phases, the
713 thermal pressure is defined by
714
715 $$P_{th} = \frac{\gamma}{V} c_V (T - T_0) \quad \text{(A.8)}$$
716
717 where $c_V$ is the isochoric heat capacity, and $\gamma$, representing the Grüneisen parameter, is a
718 function of volume as follows
719
720 $$\gamma = \gamma_0 + \gamma' \left( \frac{V}{V_0} - 1 \right) \quad \text{(A.9)}$$
721
722 where $\gamma_0$ is the Grüneisen parameter at the reference conditions and $\gamma'$ is its first
723 derivative with respect to the volume. The thermal contribution to the Helmholtz energy
724 ($\Delta F_{th}$) of a liquid is then defined by:
725
726 $$\Delta F_{th}(V) = -S_0 (T - T_0) - c_V \left[ T \ln \left( \frac{T}{T_0} \right) - (T - T_0) \right] - c_V (T - T_0) (\gamma_0 - \gamma') \ln \left( \frac{V}{V_0} \right) + (\gamma - \gamma_0)$$
727 (A.10)
729 where $S_0$ is the standard entropy of the substance at a reference state chosen to be
730 consistent with literature data as described above (see Table A).
731

For the solid phases, a slightly different approach was used starting with the calculation of the volume at the pressure and temperature of interest ($V$). The thermal pressure of the solid phase was determined using an expression for the Debye thermal energy ($E_{th}$), that is,

$$P_{th} = \frac{\gamma}{V}\left[E_{th}(V,T) - E_{th}(V,T_0)\right] \quad \text{(A.11)}$$

and, in this case, the Grüneisen parameter is calculated as

$$\gamma = \gamma_0 \left(\frac{V}{V_0}\right)^{q_0}, \quad \text{(A.12)}$$

where $q_0$ is a constant, and the thermal internal energy ($E_{th}$) is defined by the Debye model for the lattice vibrational energy

$$E_{th} = 9nRT\left(\frac{T}{\theta}\right)^3 \int \frac{t^3}{e^t - 1} dt, \quad \text{(A.13)}$$

where $R$ is the universal gas constant, n is the number of atoms per formula unit, $t = \theta/T$, with the Debye temperature ($\theta$) calculated as

$$\theta = \theta_0 e^{\frac{\gamma_0 - \gamma}{q_0}}. \quad \text{(A.14)}$$

753

754 The corresponding expression for the thermal Helmholtz energy ($F_{th}$) of the solid phases,
755 defined as the Debye approximation of the quasi-harmonic vibrational density of states, is
756 as follows:

757

$$758 \qquad F_{\text{th}}(V) = 9nRT\left(\frac{T}{\theta}\right)^3 \int \ln\left(1 - e^{-t}\right) t^2 dt \,. \qquad \text{(A.15)}$$

759

760 The thermal contribution to the Helmholtz energy ($\Delta F_{th}$) of the solid phases between the
761 reference temperature ($T_0$) and that of interest ($T$) at the constant volume of interest ($V$), is
762 found by difference:

763

$$764 \qquad \Delta F_{\text{th}}(V) = F_{\text{th}}(V,T) - F_{\text{th}}(V,T_0) \,. \qquad \text{(A.16)}$$

765

766 The thermodynamic properties employed in the calculations of the Gibbs energy for solid
767 and liquid $Mg_2SiO_4$ and $MgSiO_3$ are summarized in Table A and are based on previous
768 compilations by de Koker and Stixrude (2009) and Stixrude and Lithgow-Bertelloni
769 (2011) for liquid and solid phases, respectively. The Helmholtz energy for liquid
770 substances at reference conditions ($F_0$) was empirically calculated from the room pressure
771 melting temperatures as explained by Liebske and Frost (2012). The reference state
772 volumes ($V_0$) and entropies ($S_0$) for the liquid end-members were slightly altered
773 compared to those reported by de Koker and Stixrude (2009) in order to obtain better
774 agreement with the experimental melting temperatures and to be consistent with
775 calorimetric data for the enthalpy of melting of $MgSiO_3$ and $Mg_2SiO_4$ (Navrotsky et al.,

776 1989; Richet et al., 1993). Specifically, the thermodynamic data of $Mg_2SiO_4$ liquid of de
777 Koker and Stixrude (2009) had to be modified such that the value of $\Delta_m S^o$ for forsterite at
778 1 bar was consistent with 52.7 J/(K·mol) proposed by Navrotsky et al. (1989). This is at
779 the lower end of the range of values reported in the literature, which vary from 70 to 47.5
780 J/(K·mol) (Bottinga, 1985; Navrotsky et al., 1989; Richet et al., 1993; Tangeman et al.,
781 2001). Values for the standard heat capacity and volume of $Mg_2SiO_4$ liquid were then also
782 adjusted to bring the model into agreement with experimental data on the melting curve
783 of $Mg_2SiO_4$ (Davis and England, 1964; Kato and Kumazawa, 1985; Presnall and Walter,
784 1993).
785
786 **References**

787 Balta J.B., Asimow P.D. and Mosenfelder J.L. (2011) Hydrous, low-carbon melting of
788 garnet peridotite, *J. Petrol.* **52**, 2079–2105.
789 Bercovici D. and Karato S.-I. (2003) Whole-mantle convection and the transition-zone
790 water filter. *Nature* **425**, 39–44.
791 Brey G.P., Köhler T. and Nickel K.G. (1990) Geothermobarometry in four-phase
792 lherzolites I. Experimental Results from 10 to 60 kb. *J. Petrol.* **31**, 1313–1352.
793 Birch F. (1947) Finite elastic strain of cubic crystals. *Phys. Rev.* **71**, 809–824.
794 Bottinga Y. (1985) On the isothermal compressibility of silicate liquids at high pressure.
795 *Earth Planet. Sci. Lett.* **74**, 350–360.
796 Brooker R., Holloway J. and Hervig R. (1998) Reduction in piston cylinder experiments:
797 the detection of carbon infiltration into platinum capsules. *Am. Mineral.* **83**, 985-
798 994.

799 Burnham C.W. (1975) Water and magmas; a mixing model. *Geochim. Cosmochim. Acta*
800 **39**, 1077–1084.
801 Burnham, C.W. (1979) The importance of volatile constituents. In: *The Evolution of the*
802 *Igneous Rocks* (ed. H.S. Jr. Yoder). Princeton Univ. Press, Princeton, NJ. pp. 439–
803 482.
804 Burnham, C.W. (1994) Development of the Burnham model for prediction of $H_2O$
805 solubility in magmas. In: *Volatiles in Magmas* (eds. M.R. Carroll and J.R.
806 Holloway). Reviews in Mineralogy **30**, Mineralogical Society of America,
807 Washington D.C.
808 Dalton, J.A. and Presnall, D.C. (1997) No liquid immiscibility in the system $MgSiO_3$-
809 $SiO_2$ at 5.0 GPa. *Geochim. Cosmochim. Acta* **61**, 2367–2373.
810 Davis B.T.C. and England J.R. (1964) The melting of forsterite up to 50 kilobars. *J.*
811 *Geophys. Res.* **69**, 1113–1116.
812 de Koker N. and Stixrude L. (2009) Self-consistent thermodynamic description of silicate
813 liquids, with application to the shock melting of MgO periclase and $MgSiO_3$
814 perovksite. *Geophys. J. Internat.* **178**, 162–179.
815 Dixon J.E. and Stolper E.M. (1995) An experimental study of water and carbon dioxide
816 solubilities in mid-ocean ridge basaltic liquids. Part II: Applications to degassing.
817 *J. Petrol.*, **36**, 1633–1646.
818 Erlank E.J., Waters F.G., Hawkesworth C.J. Haggerty S.E., Allsopp H.L., Rickard R.S.
819 and Menzies M. (1987) Evidence for mantle metasomatism in peridotite nodules
820 from Kimberly pipes, South Africa. In: *Mantle Metasomatism* (eds. M.A. Menzies
821 and C.J. Hawkesworth). Academic Press, London, pp. 313–361.

822 Frost D.J., Poe B.T., Tronnes R.G., Liebske C., Duba A. and Rubie D.C. (2004) A new
823 large-volume multianvil system. *Phys. Earth Planet. Int.* **143–144**, 507–514.
824 Gaetani G.A. and Grove T.L. (1998) The influence of water on melting of mantle
825 peridotite. *Contrib. Mineral. Petrol.* **131**, 323–346.
826 Hirose K. and Kawamoto T. (1995) Hydrous partial melting of lherzolite at 1 GPa: the
827 effect of $H_2O$ on the genesis of basaltic magmas. *Earth Planet. Sci. Lett.* **133**,
828 463–473.
829 Hirschmann M.M., Tenner T., Aubaud C. and Withers A.C. (2009) Dehydration melting
830 of nominally anhydrous mantle: The primacy of partitioning. *Phys. Earth Planet.*
831 *Int.* **176**, 54–68.
832 Hodges F.N. (1973) Solubility of $H_2O$ in forsterite melt at 20 kbar. *Carnegie Inst.*
833 *Washington Yearb.* **72**, 495–497.
834 Hodges F.N. (1974) The solubility of $H_2O$ in silicate melts. *Carnegie Inst. Washington*
835 *Yearb.* **73**, 251–255.
836 Inoue T. (1994) Effect of water on the melting phase-relations and melt composition in
837 the system $Mg_2SiO_4$-$MgSiO_3$-$H_2O$ up to 15 GPa. *Phys. Earth Planet. Int.* **85**, 237–
838 263.
839 Jasbinsek, J.J., Dueker, K.G. and Hansen, S.M. (2010) Characterizing the 410 km
840 discontinuity low-velocity layer beneath LA RISTRA array in the North American
841 Southwest. *Geochem. Geophys. Geosys.* **11**, doi:10.1029/2009GC002836.
842 Jing Z. and Karato S-I. (2009) The density of volatile bearing melts in the Earth's deep
843 mantle: The role of chemical composition. *Chem. Geol.* **262**, 100–107.

844 Kato T. and Kumazawa M. (1985) Melting and phase relations in the system $Mg_2SiO_4$-
845 $MgSiO_3$ at 20 GPa under hydrous conditions. *J. Geophys. Res.* **91**, 9351–9355.
846 Kawamoto T. and Holloway J.R. (1997) Melting temperature and partial melt chemistry
847 of $H_2O$-saturated mantle peridotite to 11 GPa. *Science* **276**, 240–243.
848 Kojitani H. and Akaogi M. (1997) Melting enthalpies of mantle peridotite: calorimetric
849 determinations in the system CaO-MgO-$Al_2O_3$,-$SiO_2$ and application to magma
850 generation. *Earth Planet Sci. Lett.* **153**, 209–222.
851 Kushiro I. (1972) Effect of water on the composition of magmas formed at high
852 pressures. *J. Petrol.* **13**, 311–334.
853 Kushiro I. and Yoder H.S.Jr. (1969) Melting of forsterite and enstatite at high pressures
854 and hydrous conditions. *Carnegie Inst. Washington Yearb.* **67**, 153–158.
855 Kushiro I., Yoder H.S.Jr. and Nishikawa, M. (1968) Effect of water on the melting of
856 enstatite. *Geol. Soc. Am. Bull.* **79**, 1685–1692.
857 Lambert I. B. and Wyllie P. J. (1970) Low-velocity zone of the Earth's mantle; incipient
858 melting caused by water. *Science* **169**, 764–766.
859 Lesne P., Scaillet B., Pichavant M., Iacono-Marziano G. and Beny J.M. (2011) The $H_2O$
860 solubility of alkali basaltic melts: an experimental study. *Contrib. Mineral. Petrol.*
861 **162**, 133–151.
862 Liebske C. and Frost D.J. (2012) Melting phase relations in the MgO–$MgSiO_3$ system
863 between 16 and 26 GPa: Implications for melting in Earth's deep interior. *Earth*
864 *Planet Sci. Lett.* **345–348**, 159–170.

865 Liu X., O' Neill H.St.C., and Berry A.J. (2006) The effects of small amounts of $H_2O$, $CO_2$
866 and $Na_2O$ on the partial melting of spinel lherzolite in the system CaO-MgO-
867 $Al_2O_3$-$SiO_2$±$H_2O$±$CO_2$±$Na_2O$ at 1.1 GPa. *J. Petrol.* **47**, 409–434.
868 Luth R.W. (1993) Melting in the $Mg_2SiO_4$-$H_2O$ system at 3 to 12 GPa. *Geophys. Res. Let.*
869 **20**, 233–235.
870 Matsukage K.N., Jing Z. and Karato S-I. (2005) Density of hydrous silicate melt at the
871 conditions of Earth's deep upper mantle. *Nature* **438,** 488–491.
872 Médard E. and Grove T.L. (2008) The effect of $H_2O$ on the olivine liquidus of basaltic
873 melts: experiments and thermodynamic models. *Contrib. Mineral. Petrol*. **155**,
874 417–432.
875 Menzies M.A. and Hawkesworth C.J. (1987) *Mantle metasomatism*. Academic press,
876 London.
877 Mibe K., Fujii T. and Yasuda M. (2002) Composition of acqueous fluid coexisting with
878 mantle minerals at high pressure and its bearing on the differentiation of the
879 Earth's mantle. *Geochim. Cosmochim. Acta* **66**, 2273–2285.
880 Mierdel K., Keppler H., Smyth J.R. and Langenhorst F. (2007) Water solubility in
881 aluminous orthopyroxene and the origin of Earth's asthenosphere. *Science* **315**,
882 364-368.
883 Murnaghan, F. D. (1937) Finite deformations of an elastic solid. *Amer. J. Math.* **49**, 235–
884 260.
885 Myhill, R., Frost, D.J. and Novella, D. (2016) Hydrous melting and partitioning in and
886 above the mantle transition zone: insights from water-rich MgO-$SiO_2$-$H_2O$

887 experiments. *Geochim. Cosmochim. Acta,*
888 http://dx.doi.org/10.1016/j.gca.2016.05.027.
889 Mysen B.O. and Boettcher A.L. (1975) Melting of hydrous mantle I. Phase relations of
890 natural peridotite at high pressures and temperatures with controlled activities of
891 water, carbon dioxide, and hydrogen, *J. Petrol.* **16**, 520–548.
892 Navrotsky A., Ziegler D., Oestrike R. and Maniar P. (1989) Calorimetry of silicate melts
893 at 1773 K - measurement of enthalpies of fusion and of mixing in the systems
894 diopside-anorthite-albite and anorthite-forsterite. *Contrib. Mineral. Petrol.* **101**,
895 122–130.
896 Novella D. and Frost D.J. (2014) The composition of hydrous partial melts of garnet
897 peridotite at 6 GPa: implications for the origin of group II kimberlites. *J. Petrol.*
898 **5**, 2097–2124.
899 Novella D., Frost D.J., Hauri E.H., Bureau H., Raepsaet C. and Roberge M. (2014) The
900 distribution of water between nominally anhydrous peridotite and melts in the
901 Earth's upper mantle. *Earth Planet Sci. Lett.* **400**, 1–13.
902 Nowak M. and Behrens H. (1995) An in situ near infrared spectroscopic study of water
903 speciation in haplogranitic glasses and melts. *Fifth Silicate Melt Work-shop*
904 *Program and Abstracts*, La Petite Pierre, France.
905 Pamato M., Myhill, R., Boffa Ballaran T., Frost D.J., Heidelbach F. and Miyajima N.
906 (2015) Lower-mantle water reservoir implied by the extreme stability of a
907 hydrous aluminosilicate. *Nature Geoscience* **8**, 75–79.
908 Poirier J.P. (2000) Introduction to the physics of the Earth interior. 2nd ed, Cambridge
909 University Press, Cambridge.

910 Presnall D.C. and Walter M.J. (1993) Melting of forsterite, $Mg_2SiO_4$, from 9.7 to 16.5
911 GPa. *J. Geophys. Res.* **98**, 19777–19783.
912 Rauch, M. and Keppler, H. (2002). Water solubility in orthopyroxene. *Contrib. Mineral.*
913 *Petrol.* **143**, 525–536.
914 Richet P., Robie R.A. and Hemingway B.S. (1993) Entropy and structure of silicate
915 glasses and melts. *Geochim. Cosmochim. Acta* **57**, 2751–2766.
916 Ross N.L., Akaogi M., Navrotsky A., Susaki J., and McMillan P. (1986) Phase
917 transformations among $CaGeO_3$ polymorphs (wollastonite, garnet, and perovskite
918 structures): studies by high-pressure synthesis, high-temperature calorimetry and
919 vibrational spectroscopy and calculation. *J. Geophys. Res.* **91**, 4601–1696.
920 Schmandt B., Jacobsen S.D., Becker T.W., Liu Z. and Dueker K.G. (2014) Dehydration
921 melting at the top of the lower mantle. *Science* **344**, 1265–1268.
922 Silver L.A. and Stolper E.M. (1985) A thermodynamic model for hydrous silicate melts.
923 *J. Geol.* **93**, 161–178.
924 Silver L.A. and Stolper E.M. (1989) Water in albitic glasses. *J. Petrol.* **30**, 667–709.
925 Sokol A.G., Kupriyanov I.N., Palyanov Y.N., Krunk A.N. and Sobolev N.V. (2013)
926 Melting experiments on the Udachnaya kimberlite at 6.3-7.5 GPa: Implications
927 for the role of $H_2O$ in magma generation and formation of hydrous olivine.
928 *Geochim. Cosmochim. Acta* **101**, 133–155.
929 Song, A.T-R., Helmberger, D.V. and Grand, S.P. (2004) Low-velocity zone atop the 410-
930 km seismic discontinuity in the northwestern United States. *Nature* **427**, 530–533.
931 Stixrude L. and Linthgow-Bertelloni C. (2011) Thermodynamics of mantle minerals – II.
932 Phase equilibria. *Geophys. J. Int.* **184**, 1180–1213.

933 Stolper E. (1982) Water in silicate glasses: an infrared spectroscopy study. *Contrib.*
934 *Mineral. Petrol.* **81**, 1–17.
935 Takahashi E. (1986) Melting of dry peridotite KLB-1 up to 14 GPa: implications on the
936 origin of peridotitic upper mantle. *J. Geophys. Res.* **91**, 9367–9382.
937 Tangeman J.A., Lange R., and Forman L. (2001) Ferric-ferrous equilibria in $K_2O$-FeO-
938 $Fe_2O_3$-$SiO_2$ melts. *Geochim. Cosmochim. Acta* **65** 1809–1819.
939 Tatsumi Y., Hamilton D.L. and Nesbitt R.W. (1986) Chemical characteristics of fluid
940 phase released from a subducted lithosphere and origin of arc magmas: Evidence
941 from high-pressure experiments and natural rocks. *J. Volcan. Geotherm. Res.* **29**,
942 293–309.
943 Tauzin B., Debayle E. and Wittlinger G. (2010) Seismic evidence for a global low-
944 velocity layer within the Earth's upper mantle. *Nature Geoscience* **3**, 718–721.
945 Tenner T.J., Hirschmann M.M. and Humayun M. (2012a) The effect of $H_2O$ on partial
946 melting of garnet peridotite at 3.5 GPa. *Geochem. Geophys. Geosys.* **13**,
947 doi:10.1029/2011GC003942.
948 Tenner, T.J., Hirschmann, M.M., Withers, A.C. and Ardia, P. (2012b) $H_2O$ storage
949 capacity of olivine and low-Ca pyroxene from 10 to 13 GPa: consequences for
950 dehydration melting above the transition zone. *Contrib. Mineral. Petrol.* **163**,
951 297–316.
952 Vinnik, L., Oreshin, S., Kosarev, G., Kiselev, S. and Makeyeva, L. (2009) Mantle
953 anomalies beneath southern Africa: evidence from seismic S and P receiver
954 functions. *Geophys. J. Int.* **179**, 279–298.

955 Walter M.J. (1998) Melting of garnet peridotite and the origin of komatiite and depleted
956 Lithosphere. *J. Petrol.* **39**, 29–60.
957 Withers, A.C. and Hirschmann, M.M. (2007) $H_2O$ storage capacity of $MgSiO_3$ clino-
958 enstatite at 8–13 GPa, 1100–1400 °C. *Contrib. Mineral. Petrol.* **154**, 663–674.
959 Withers, A.C., Hirschmann, M.M. and Tenner, T. (2011) The effect of Fe on olivine $H_2O$
960 storage capacity: consequences for $H_2O$ in the Martian mantle. Am. Mineral 96,
961 1039–1053.
962 Yamada A., Inoue T. and Irifune T. (2004) Melting of enstatite from 13 to 18 GPa under
963 hydrous conditions. *Phys. Earth Planet. Int.* **147**, 45–56.
964 Zotov N. and Keppler H. (1998) The influence of water on the structure of hydrous
965 sodium tetrasilicate glasses. *Am. Mineral.* **83**, 823–834.
966

967 **Figure captions**

968 **Fig. 1**: Backscattered electron (BSE) images of experiments performed at 6 GPa in the
969 $Mg_2SiO_4$-$H_2O$ system. The bright material is the Pt capsule. Grey crystals (50 to 100 μm
970 across) of forsterite can be easily distinguished from the fine grain quenched melt. (**a**):
971 figure corresponds to experiment V649 (Table 2) where in order from left to right are
972 sample chambers containing starting mixtures of $Mg_2SiO_4$ plus 5, 10, 15 and 20.4 wt%
973 $H_2O$ in the bulk. The third chamber from the left shows two quench textures in the same
974 charge with different fibrous grain sizes, likely formed due to differences in nucleation
975 and crystal growth (see text). (**b**): BSE image of experiment V660 (Table 2) where, from
976 left to right, starting mixtures of $Mg_2SiO_4$ with 7.9, 9.7, 13.8 and 18.3 wt% $H_2O$ (bulk)
977 were employed.

978 **Fig. 2**: Phase diagram of the $Mg_2SiO_4$-$H_2O$ system at 6 GPa showing experimental data
979 and models for the liquidus curves (described in the text). Data points determined in this
980 study are displayed by black and grey symbols (Table 2) while data from Luth (1993) at 6
981 GPa and Inoue (1994) at 5.5 GPa are shown by blue and green symbols, respectively.
982 Data from Luth (1993) and Inoue (1994) were determined for bulk compositions of
983 $Mg_2SiO_4$ plus 20.4 wt% $H_2O$ but are plotted at slightly higher $H_2O$ content to aid
984 visibility. The liquidus at approximately 20 wt% $H_2O$ is ~200 °C lower than reported by
985 Inoue et al. (1994) at 5.5 GPa but is in agreement, within uncertainty, with the data of
986 Luth (1993) at 6 GPa. The plotted liquidus curves are all constrained by the dry melting
987 temperature of forsterite at 6 GPa reported by Kato and Kumazawa (1985). Details
988 regarding the different curves are reported in the text. Uncertainties of 1 wt% in the melt
989 composition and 50-100 °C for the temperature of the experiments (see text) are
990 displayed by the error bars.

991 **Fig. 3**: Indicative ternary phase diagrams in the system MgO-$SiO_2$-$H_2O$. Phase relations
992 are tentatively constrained at 6 (top) and 13 (bottom) GPa by the experimental results
993 reported in this study and the literature. Starting compositions in the forsterite-$H_2O$ and
994 enstatite-$H_2O$ joins are plotted as black circles, on a molar basis. Fo: forsterite; En:
995 enstatite; Per: periclase; St: stishovite; L: liquid (or melt). The dashed line indicates the
996 Fo + En = L reaction curve while the dotted lines show the possible location of the Fo +
997 Per = L (toward MgO corner) and En + St = L (toward $SiO_2$ corner) curves.

998 **Fig. 4**: The depression of the $MgSiO_3$ liquidus curve at 6 GPa as a function of melt $H_2O$
999 content. Data points determined in this study (Table 2) are displayed by black symbols
1000 while green symbols are from Inoue (1994), plotted at slightly higher $H_2O$ content to aid

1001 visibility. Uncertainties of 1 wt% in the melt composition and 50-100 °C for the
1002 temperature of the experiments (see text) are displayed by the error bars. Curves
1003 describing the liquidus determined by different models as described in the text are also
1004 shown. The liquidus curves are all constrained by the dry melting temperature of enstatite
1005 at 6 GPa reported by Kato and Kumazawa (1985).

1006 **Fig. 5**: Melting phase relations in the $Mg_2SiO_4$-$H_2O$ system at 13 GPa. Uncertainties of 1
1007 wt% in the melt composition and 50-100 °C for the temperature of the experiments (see
1008 text) are displayed. The dry melting temperature of forsterite at 13 GPa was calculated to
1009 be 2200 °C by extrapolation of the equations of state of de Koker and Stixrude (2009).

1010 **Fig. 6**: The melting phase relations in the $MgSiO_3$-$H_2O$ system at 13 GPa. Uncertainties
1011 of 1 wt% in the melt composition and 50-100 °C for the temperature of the experiments
1012 (see text) are displayed. The dry melting temperature of enstatite at 13 GPa was
1013 calculated to be 2250°C using the model of de Koker and Stixrude (2009). Values of $a$ =
1014 -8000 K and $b$ = 8 were employed in the calculation of constant $K$ (red line).

1015 **Fig. 7:** The depression in the hydrous melting temperature as a function of $H_2O$ for
1016 $MgSiO_3$-$H_2O$ (black lines), $Mg_2SiO_4$-$H_2O$ (green lines) and natural (blue lines) melt
1017 compositions between 1 and 13 GPa. Hydrous garnet peridotite melt compositions are
1018 from Tenner et al. (2012a) at 3.5 GPa (red dots) and Novella and Frost (2014) at 6 GPa
1019 (grey square). The blue curves are fitted to these data, as described in the text.

1020 **Fig. 8:** Melt $H_2O$ contents as a function of pressure determined at 3.5, 6 and 13 GPa and
1021 at temperatures corresponding to a mantle adiabat (1350 °C, 1400 °C and 1500 °C,
1022 respectively). Peridotite data are taken from the curves shown in Fig. 7.